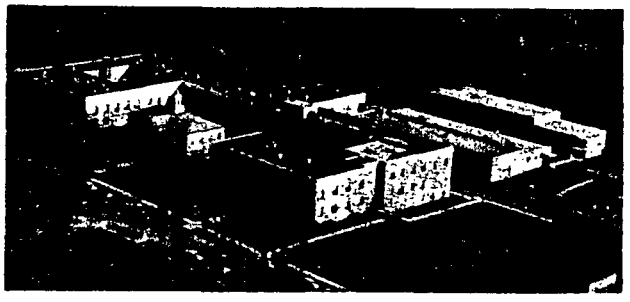

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

RESEARCH ON SMELT-WATER REACTIONS

Report Three

1. Third Activity Report of Project Co-ordinator, IPC Project 2419, to Advisory Technical Committee
2. Progress Report of The Babcock & Wilcox Company to August 14, 1964
3. Progress Report of Combustion Engineering, Inc. to August 15, 1964

September 4, 1964

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

THIRD ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

Project 2419

August 28, 1964

This research project is being conducted for the Board of Directors created by a group of manufacturers of chemically produced wood pulp, pursuant to Sponsorship Agreements (this group of companies hereinafter referred to as the Smelt-Water Research Group). This report, or any portions thereof, may not be quoted, reproduced, or disseminated outside the member companies of the Smelt-Water Research Group without the express written approval of the Advisory Technical Committee, The Babcock & Wilcox Company, Combustion Engineering, Inc., and The Institute of Paper Chemistry.

In view of the tentative nature of research results and the early stage of the research here reported, readers are cautioned against drawing premature conclusions and are advised to await definite recommendations which will be offered when the significance of the technical work has been confirmed and conclusions become warranted.

Distribution:

Board of Directors
Advisory Technical Committee
Fourdrinier Kraft Board Institute – Messrs. Boren, Rea
The Babcock & Wilcox Company – Messrs. Darmstadt, Markant (3), Moran
Combustion Engineering, Inc. – Messrs. Hochmuth, Lawlor, Nelson (2), Ulmer
The Institute of Paper Chemistry – Messrs. Smith, Strange, Whitney

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

THIRD ACTIVITY REPORT OF PROJECT CO-ORDINATOR

This report covers activities of the Project Co-ordinator from June 24 to August 28. Work by the research organizations of The Babcock & Wilcox Company and of Combustion Engineering, Inc. is presented in attached reports, and covers the period from May 12 through August 14.

The work reported from the laboratories of the boiler companies continues to add to knowledge of the mechanism of explosions caused by contact of smelt and water in recovery furnaces. The Babcock & Wilcox Company work indicates the possibilities for generating hydrogen, carbon monoxide, hydrogen sulfide, and possibly other combustible gases. Further work will define more precisely the conditions under which these gases are formed. Whether or not they prove to be the primary factor in the mechanism of actual furnace smelt-water explosions, their presence will have to be considered and their contribution to explosions will have to be determined by further study.

The laboratory work at Combustion Engineering, Inc. has developed the ability to produce smelt-water explosions on a small scale. It appears that these explosions are primarily physical in nature, that they occur in a manner which is consistent with the theoretical concept of an encapsulation mechanism, and that the explosions are greatly influenced by the physical conditions and the chemical composition of the smelt and the water or solution with which it interacts. The detection of small amounts of hydrogen before the explosions at Combustion Engineering, Inc. confirms the probability of chemical reaction between water and smelt, but it seems likely that these chemical reactions may not be significant in the explosions being produced currently at Combustion Engineering, Inc. From the

work on the physical mechanism of smelt-water explosions, it appears that this concept is consistent with our general knowledge of recent furnace explosions of this type. However, we cannot yet explain in detail, and may never be able to explain with certainty, the way in which liquid water becomes encapsulated by smelt under furnace conditions. Because this problem is so important, studies by The Babcock & Wilcox Company of furnace chemistry and the conditions which prevail within operating char beds are of particular significance.

On June 27 and 28, the Project Co-ordinator visited the plant of Bowaters Carolina Corporation, Catawba, South Carolina, where a recovery furnace explosion had occurred on June 23. The co-operation of the plant management in freely supplying information for our consideration is greatly appreciated. Although a screen tube failure initiated the series of events leading to the explosion, the mechanism of the explosion has not been conclusively established.

As a member of the Subcommittee on Emergency Shut Down Procedures of the Black Liquor Recovery Boiler Advisory Committee, the Project Co-ordinator attended a subcommittee meeting in Seattle on July 29. Contact with this program is continuing to provide useful information for the smelt-water research effort.

On August 15, 16, and 25, while on a previously scheduled vacation trip, the Project Co-ordinator visited the plant of Fibreboard Paper Products Corporation, East Antioch, California to obtain information regarding a bottom tube failure which had occurred on August 13. The incident had developed a pool of water in a corner of the hearth, but emergency shutdown procedure was carried out successfully. The co-operation of the Fibreboard Paper Products Corporation management in developing useful information was most helpful.

Because of the urgent need for a prompt solution to the smelt-water explosion problem, an effort is being made to establish contact with whatever sources of information or experience are likely to be helpful. On August 19 and 21, the Project Co-ordinator visited Stanford Research Institute, Menlo Park, California to explore the possibility of effective contribution to the problem by Stanford Research Institute. The matter is currently under consideration by certain Stanford Research Institute staff members, and may be developed further to the point of a research proposal, if it appears that such consideration might be justified.

At the present time, the Project Co-ordinator believes that both physical and chemical reactions between smelt and water must be better understood, particularly as they relate to actual furnace conditions. However, the present information is sufficient to justify recognition of the possibility of very real danger whenever smelt and water are both present in a recovery furnace. In the light of our greater understanding of the danger, we should begin consideration of preventive measures as soon as there appears to be any possibility of constructive action.

Howard S. Gardner
Project Co-ordinator
The Institute of Paper Chemistry
Appleton, Wisconsin

PROGRESS REPORT

FOR THE PERIOD OF MAY 13, 1964 TO AUGUST 14, 1964

TO

H. S. GARDNER, PROJECT COORDINATOR,
THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

THE BABCOCK & WILCOX COMPANY
RESEARCH CENTER
ALLIANCE, OHIO

September 1, 1964

PROGRESS REPORT OF THE BABCOCK & WILCOX COMPANY
ACTIVITIES ON INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

This report summarizes the work accomplished between May 13 and August 14, 1964 and the present status of this project. Our objective, as outlined in our first progress report, is to determine what chemical reactions take place between the smelt/char-combustion gas system with water and/or steam that result in subsequent explosive reactions. Our ultimate objective is to determine the critical conditions which result in explosions so that preventative measures and shut-down procedure can be outlined on a firm scientific basis.

STATUS

Background Studies

All of the pertinent literature has been reviewed. In addition, our preliminary conclusion concerning the earlier B&W experimental work has been strengthened by a search of our files for additional data. Although a number of gas samples from the test furnace were taken before the addition of water, we can find in our records only two analyses. Both showed the presence of significant amounts of oxygen before, and smaller amounts of oxygen as well as residual hydrogen, after the explosion.

The information available from our files on actual smelt-water explosions has been reviewed. Although our information in some instances is not as complete as we would like, there are some features which appear significant. In some instances there was a time delay of as long as 2-3 hours after the first, initial explosion before additional explosions occurred; most occurred after shutdown had been initiated. Such instances suggest that explosions may occur by two different mechanisms; an initial explosion caused by water in the smelt and a

secondary explosion possibly resulting from black liquor quenching. In this latter connection our attention has been drawn to the work of Rabinovitch, Luner, James, and Gauvin[1] dealing with the pyrolysis of spent calcium sulfite liquor. This work showed that large amounts of combustible gases were formed during the pyrolysis, and conversation with J. J. O. Gravel of the Pulp and Paper Research Institute of Canada confirms that this also occurs with Kraft liquors. Because of the implication that black liquor quenching of the bed may result in the release of large amounts of combustible gases, it appears that both mechanisms must be considered.

As a further generality, observed damage has been more extensive in the central and upper parts of the furnace than at the bottom.

The literature pertaining to shock waves and to damage analysis is being reviewed. In this regard we have visited Dr. van Dolah and his associates of the Bureau of Mines who were able to give us valuable advice in this area.

Field Studies

As an adjunct to our literature review and laboratory studies, in order to obtain additional factual information on conditions existing in an operating Kraft recovery unit, our program includes the analysis of gas and smelt samples, along with temperature profiles, from such a unit. Two separate sets of tests have been carried out at the D. M. Bare Company. In the first set, gas samples were pulled from near the primary air ports, in the second set samples were obtained from above the hearth. The results of these tests were not conclusive but showed the presence of combustible material as high as 30 feet above the hearth. It was attempted to obtain smelt samples from the smelt bed under an inert atmosphere by means of a newly-designed smelt sampler, but no valid samples were obtained. Attempts to obtain continuous gas analyses by gas

chromatography were unsuccessful. Further field tests are planned to obtain gas and smelt samples.

Chemical Equilibrium Studies

Studies of the theoretical concentrations of the various species expected to exist under different conditions are being made and have consisted of two related approaches. The first approach is aimed at the equilibrium species to be expected from the black liquor feed under variable conditions of temperature and total air. In this case the complex equilibria and the number of species possible make it mandatory that computer techniques be utilized for the calculations. The second approach, aimed at predicting the reactions of molten smelt with water are somewhat simpler and can be readily calculated by hand.

It was mentioned in the last progress report that practically all of the thermodynamic data had been compiled. Since that time additional compilations became available to us, the JANAF Thermochemical Tables[2] and Rosen's tabulation[3]. The JANAF data appear to be the best obtainable for gaseous species and will be used. However, Rosen's data for the condensed species will be used, with the exception that Coughlin's data[4] will be used for $Na_2SO_4(V)$. It should be pointed out that the basic free energy, enthalpy and entropy data for sodium sulfide are not known with acceptable accuracy; we hope to obtain such data in the temperature range of interest as a by-product of our laboratory experiments.

Our computer program for calculating the equilibrium species by the free energy minimization procedure has been written and checked out for an all-gaseous system. As an illustrative example, and to independently check the program, the example worked out by Brinkley[5] by desk calculation and using his equilibrium constant method, was run on our program. A comparison of the results of the reaction of C_3H_8 with stoichiometric amounts of air at 40 atm and 2200°K are shown in Table I.

Table I - Comparison of Calculated Equilibrium For $C_3H_8 + 5O_2 + 20N_2 \rightarrow CO, H_2, N_2, CO_2, H_2O, H, OH, O, NO, O_2$. T = 2200°K, P = 40 atm. B&W Calculation Using JANAF Free Energy Data and Free Energy Minimization Method

	Concentration (moles/100 grams)	
	Brinkley	B&W
Species		
CO	.01102	.01048
H_2	.00290	.00274
N_2	2.6146	2.6147
CO_2	.3814	.3820
H_2O	.5182	.5193
H	.000094	.000087
OH	.004343	.002394
O	.000055	.000051
NO	.003586	.003415
O_2	.004074	.004149

It will be noted that slight discrepancies exist; these may be attributed to the older equilibrium data which Brinkley used in his example.

As of the date of this report the program had not been checked out on a system in which condensed phases are present.

Calculations of the expected reactions between smelt/char constituents and water have been carried out. The results indicate that the following reactions would be of importance in forming potentially explosive gases.

(1) $C + H_2O \rightarrow CO + H_2$

(2) $CO + H_2O \rightarrow CO_2 + H_2$

(3) $1/4\ Na_2S + H_2O \rightarrow 1/4\ Na_2SO_4 + H_2$

(4) $Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$

(5) $Na_2CO_3 + 2C \rightarrow Na_2 + 3CO$
then, $Na + H_2O \rightarrow NaOH + H_2$

(6) $Na_2CO_3 + 4C \rightarrow Na_2C_2 + 3CO$
then, $Na_2C_2 + H_2O \rightarrow Na_2O + C_2H_2$

Reaction (1) is the familiar water gas reaction and from equilibrium conditions appears to be a most probable reaction. At the temperatures under consideration (1150-2200 F) the equilibrium constants are favorable and are known with good accuracy. The log of equilibrium constant is shown as a function of temperature in Figure 1.

The water gas shift reaction (reaction 2) can also take place in this temperature region. It is an exothermic reaction and could be a source of additional hydrogen.

Reaction (3) is of interest because of the B&W experimental work in 1954 indicated such a reaction actually occurred. The solid line plotted in Figure 1 is the equilibrium calculated from Rosen's tabulation of basic thermodynamic data. Later, however, as a by-product of experimental studies of reaction (4) Rosen determined a P_{H_2}/P_{H_2O} ratio of .09 at 1000°K (1342°F). Thus it appears that a better approximation to the equilibrium constant for this reaction is that shown as a dotted line in Figure 1.

Although at first glance the equilibrium constant may not appear particularly favorable for the formation of hydrogen, it must be kept in mind that when a molten system is being considered, the activities of the condensed species as well as the partial pressures of the gaseous constituents interact to satisfy the equilibrium constant. Thus the amount of hydrogen formed by a reaction of water with sodium sulfide would be:

$$P_{H_2} = \frac{a^{1/4}_{Na_2S} \times P_{H_2O} \times K}{a^{1/4}_{Na_2SO_4}}$$

Assuming that the activities are roughly proportional to mole fractions, the partial pressure of hydrogen formed is dependent, not only on the value of the equilibrium constant and the P_{H_2O}, but also on the ratio of moles of Na_2S/moles Na_2SO_4. When it is considered that this latter ratio may be as high

as 20 (even though the yield is proportional to the 1/4th power) it appears that significant amounts of hydrogen can be generated from this reaction. The uncertainties in the thermodynamic data make it necessary to carry out laboratory experiments to determine its importance.

Reaction (4) was studied by Rosen[6] and his experimental data was used to extrapolate the equilibrium constant-temperature curve. This reaction would generate H_2S, a gas approximately as explosive as hydrogen. It is an exothermic reaction and would tend to generate H_2S at lower temperatures; however, as it is also dependent on the amount of CO_2 available, possibly from the reaction of Na_2CO_3 with water, it is difficult to predict its relative importance. The extent of this reaction will also be determined by experiment.

Reactions (5) and (6) appear to be favored at higher temperatures and reducing atmospheres and we shall initially investigate the more probable reactions (3) and (4).

Experimental Studies

Our initial experimental studies have as their main purpose the quantitative determination of the reaction products of water with smelt, with an additional objective of obtaining rates of reaction.

Our experimental apparatus has been designed and partially constructed. A sketch of our apparatus is shown in Figure 2. It consists of a silicon carbide crucible enclosed by a furnace encased in a stainless steel shell. Helium gas is bubbled through water held at a fixed temperature thus providing a means for obtaining known partial pressures of water vapor in the gas. After loading the silicon carbide crucible with the smelt constituent of interest the helium-water vapor mixture is passed into the melt via the graphite gas sparger. The gases formed by the reaction are then sampled and analyzed.

Provision is made to sample the material in the crucible; temperatures are determined by means of a thermocouple inserted in a well in the solid or liquid reactant. A photograph of the furnace section is shown in Figure 3.

Our initial tests have indicated that silicon carbide is a suitable containment vessel for molten smelt. If future work does not substantiate these results a graphite liner will be inserted in the crucible.

A procedure for preparing pure Na_2S was developed and tested. Briefly this involved the dehydration under a vacuum of $Na_2S \cdot 9H_2O$ to the pentahydrate and heating the latter material at 700°C under an atmosphere of hydrogen. Upon cooling in nitrogen, pink crystals of Na_2S were obtained that analyzed 97.5% Na_2S by the Mead titration procedure. No sulfur species other than sulfide were detected; there may have been some water remaining in the material.

WORK PLANNED AND EXPECTED PROGRESS

It is planned to continue our efforts to obtain additional data on operating recovery units and by the end of the next quarter this work should be near completion.

The computer program should have been finalized, and equilibrium compositions as a function of temperature and total air will be tabulated.

It is expected that our experimental program will be well under way during the next 3 months and the sodium sulfide-water reaction will have been studied and understood. The effect of sodium sulfate on the reaction of liquid sodium sulfide and water vapor will also have been investigated.

Because of the possible deleterious effect of black liquor quenching, if time permits, studies are planned by DTA (Differential Thermal Analysis) and TGA (Thermogravimetric Analysis) to obtain data on the heat evolved upon pyrolysis of black liquor as well as the rate at which this material decomposes.

EXPENDITURES

Labor	$11,663.59
Overhead	18,738.33
Materials*	3,732.83
Total Expenditures	$34,134.75

*Includes travel and $1837.90 purchase commitment

A cost control chart showing actual and anticipated expenditures is attached.

Submitted by: C. H. Anderson

C. H. Anderson
Research Chemist

CHA:vlr

Approved by: W. A. Keilbaugh

W. A. Keilbaugh, Chief
Chemical Section

References

(1) Rabinovitch, W., Luner, P., James, R. H. W., and Gauvin, W. H., Pulp and Paper Mag. Can. 57, Dec., 123 (1956).

(2) JANAF Thermochemical Tables, The Dow Chemical Company, Midland, Michigan, 1963.

(3) Rosen, Erik, Trans. Roy. Inst. Tech., Stockholm, No. 159 (1960).

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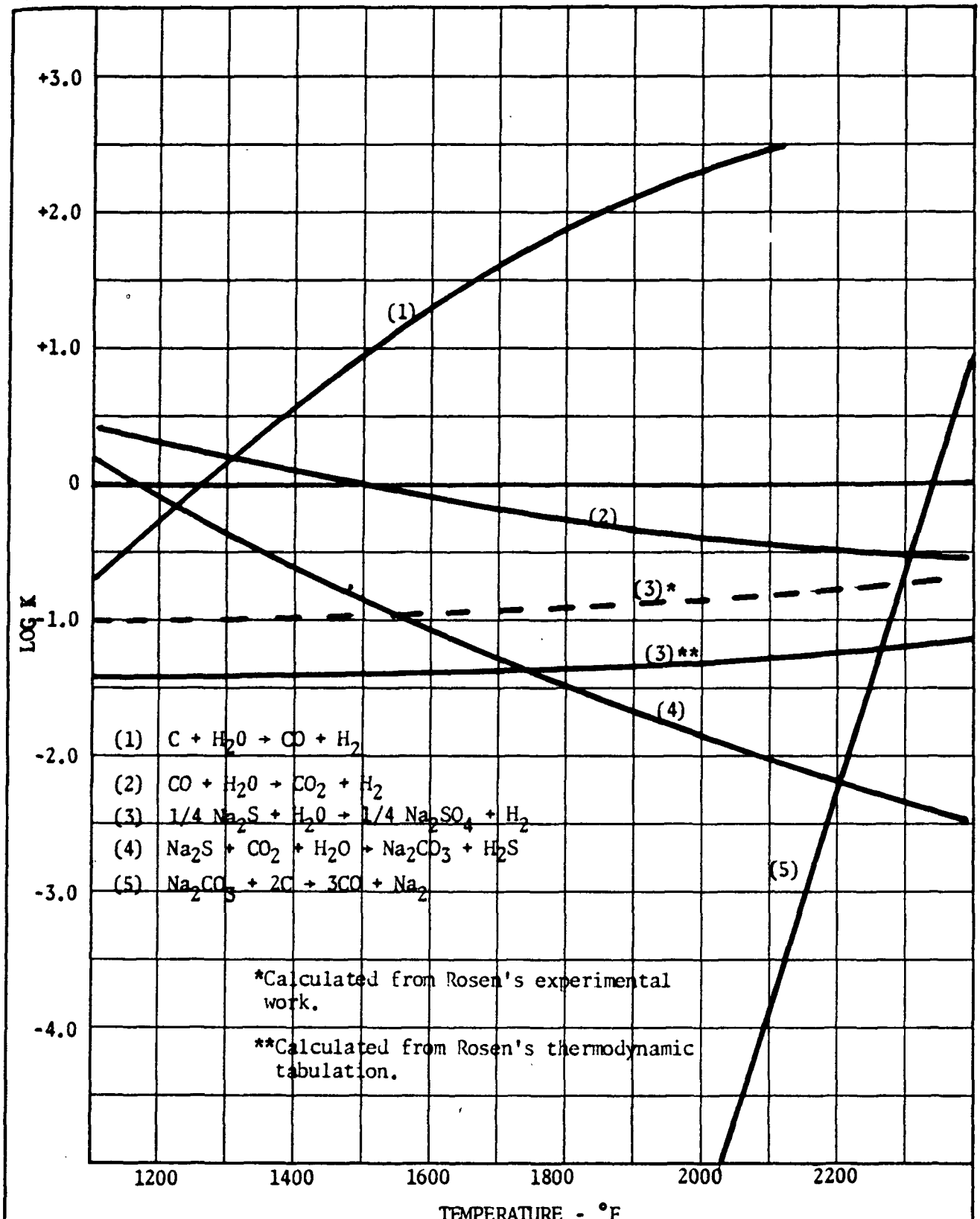
(5) Kandiner, H. J., and Brinkley, S. R., Ind. Eng. Chem., 42, No. 5, 850 (1950).

(6) Rosen, Erik, Trans. Roy. Inst. Tech., Stockholm, No. 221 (1964).



SUBJECT LOG OF EQUILIBRIUM CONSTANT AS A FUNCTION OF TEMPERATURE FOR POSSIBLE SMELT-WATER REACTIONS.	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH LABORATORY ALLIANCE, OHIO
	BY	
	DATE	
	REV.	DRAWING NO.

FIGURE 1

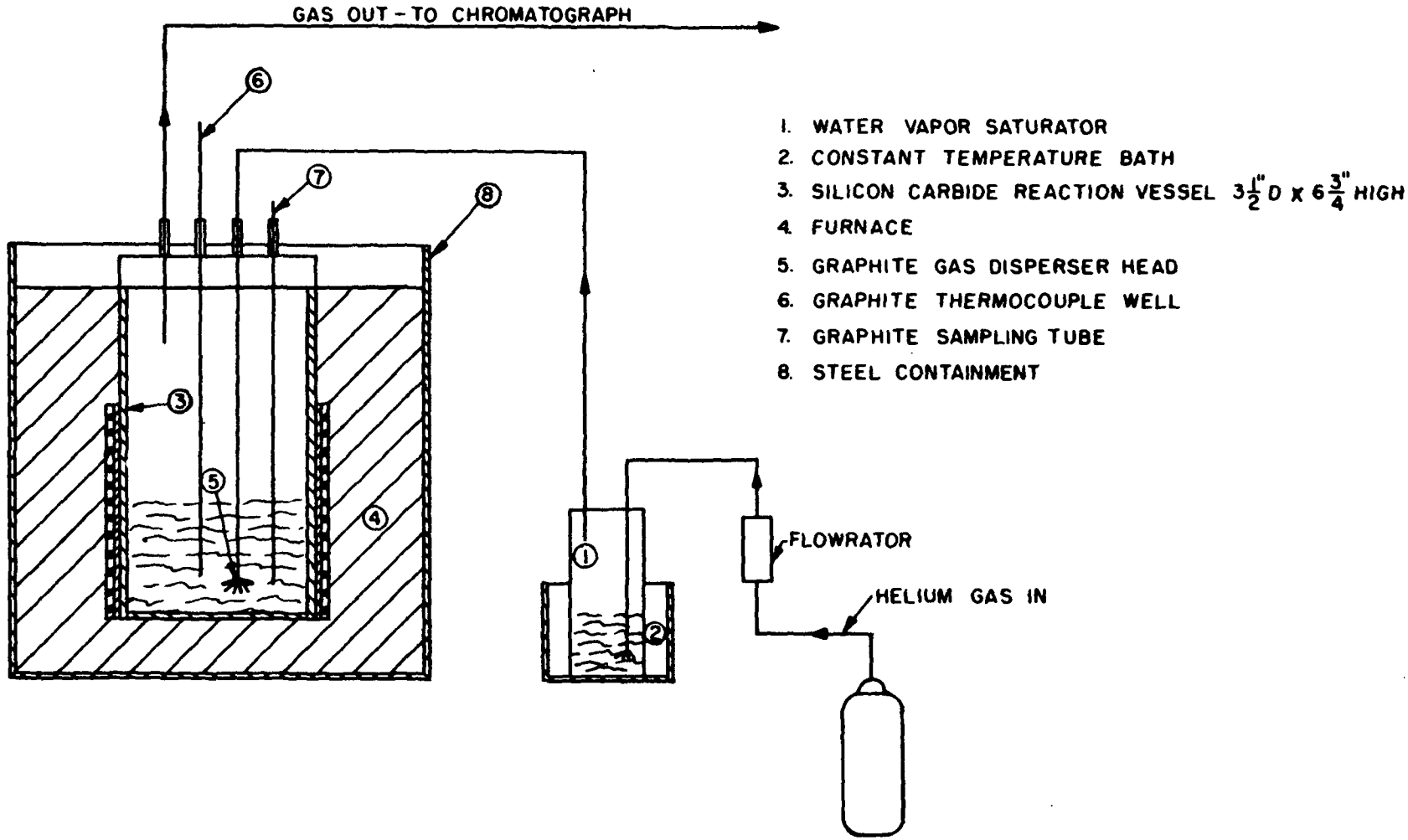
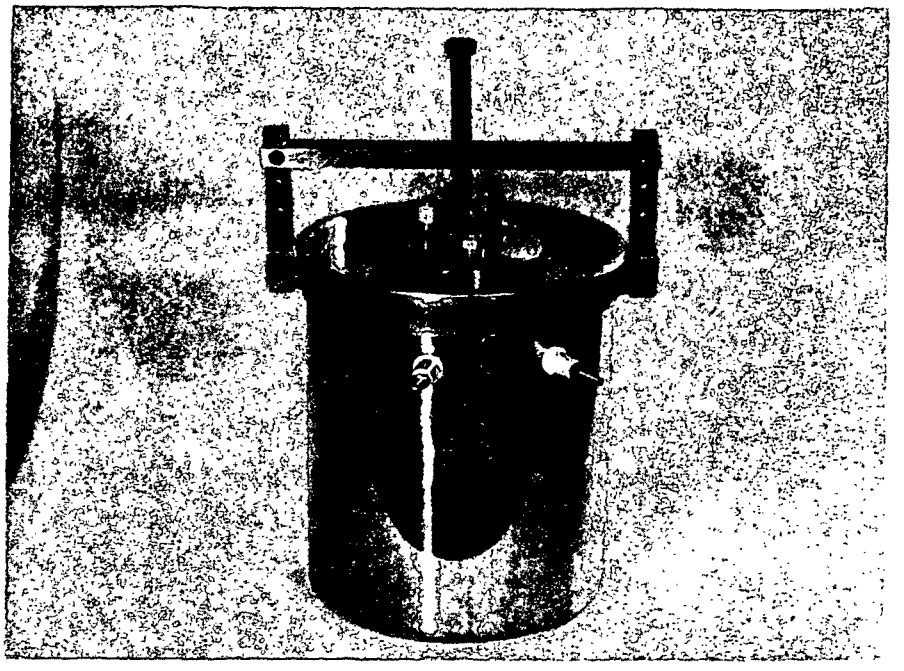
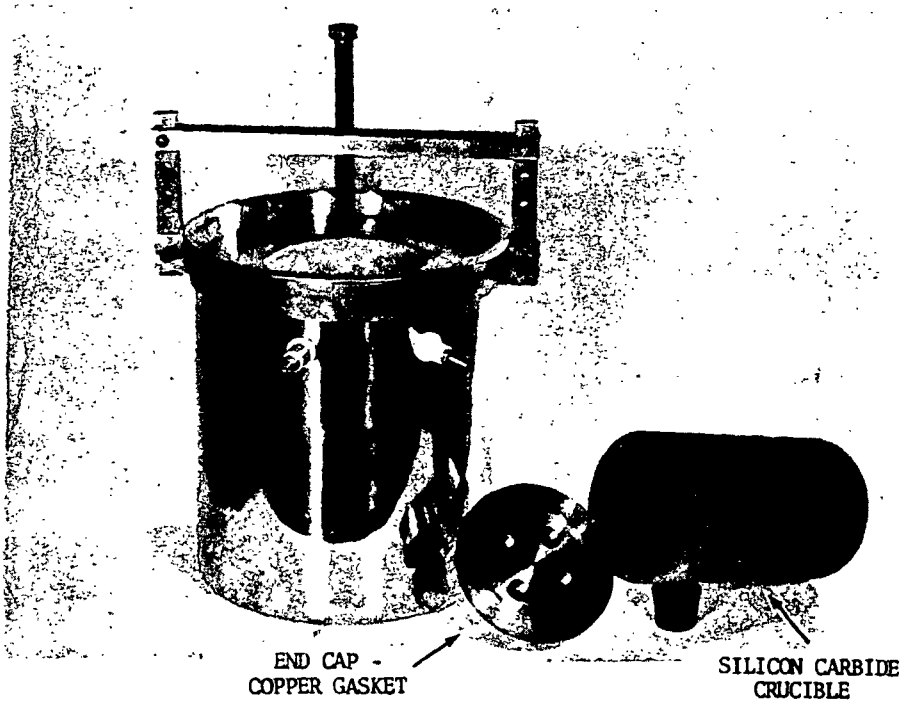


FIGURE 2

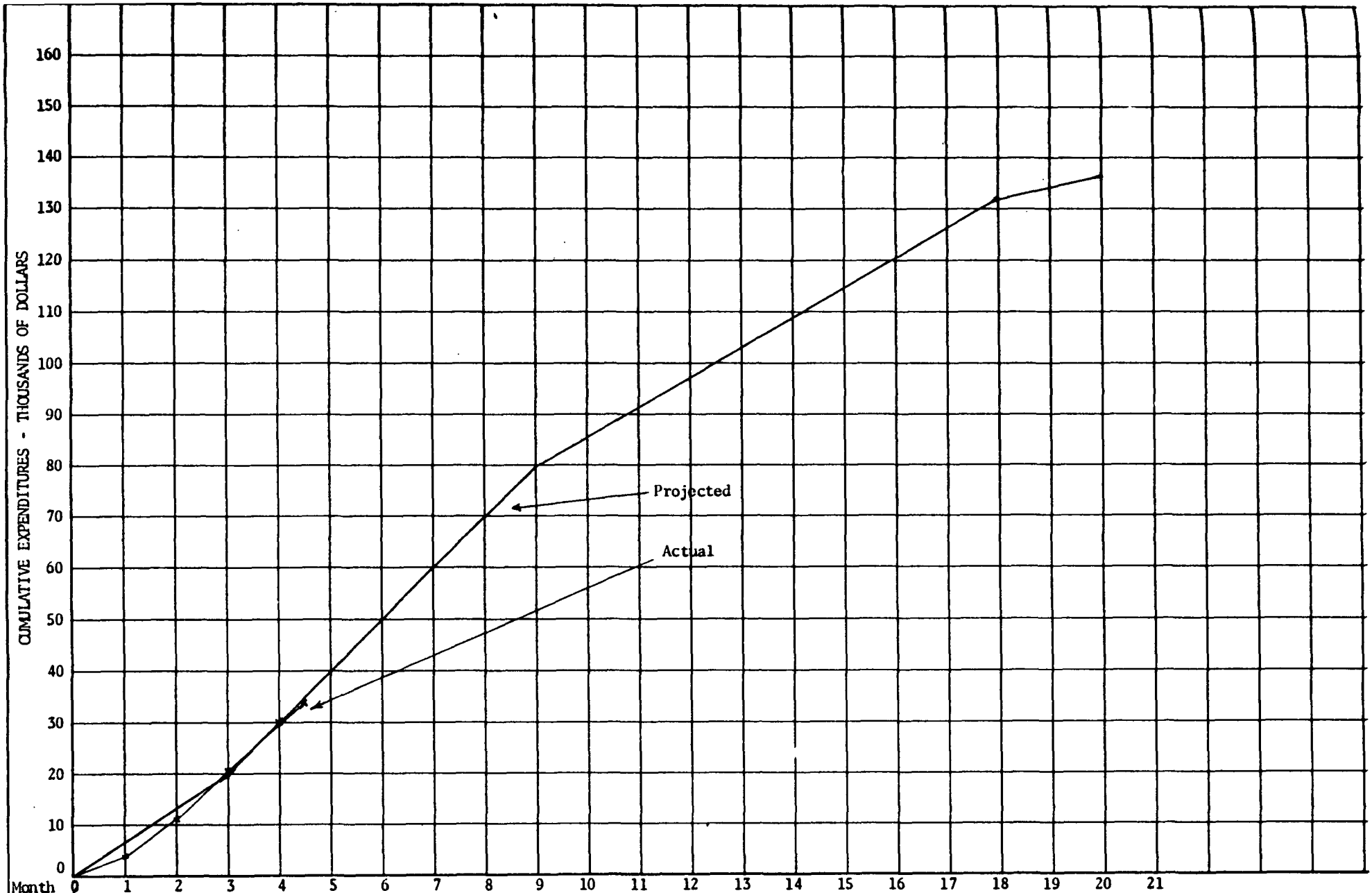
SMELT—WATER REACTION APPARATUS





SMELT-WATER REACTION APPARATUS

FIGURE 3



SUBJECT ANTICIPATED EXPENDITURE VS TIME CURVE, INVESTIGATION OF SMELT-WATER REACTIONS FOR FOURDRINIER KRAFT INSTITUTE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
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TRIMONTHLY PROGRESS REPORT
COVERING WORK FROM MAY 15 TO AUG. 15, 1964

To

Dr. H. S. Gardner, Project Coordinator
The Institute of Paper Chemistry

Submitted by
Combustion Engineering, Inc.
Kreisinger Development Laboratory
Windsor, Connecticut

NO. 2 PROGRESS REPORT ON THE COMBUSTION ENGINEERING PROGRAM FOR DETERMINING THE NATURE OF AND REMEDIES FOR EXPLOSIVE REACTION(S) BETWEEN SMELT AND WATER IN KRAFT CHEMICAL RECOVERY FURNACES

Introduction

C.E.'s previous two year laboratory and field study of explosions which occur when molten smelt tapped from a kraft chemical recovery furnace strikes water in the dissolving tank, has provided interesting parallels with the present study. The ratio of water to smelt used in these earlier experiments has been inverted for the current work so that one part of water is now injected into 10 to 500 parts of smelt as may be more likely encountered when a steam-generating tube ruptures inside the furnace.

Due to inherent uncertainties about ash bed and smelt conditions leading to explosions when water from a ruptured generating tube is introduced, it was impossible to be sure which ratio of reactants causes explosions or if they result over a wide range of smelt-to-water proportions. Figure 1 illustrates several possible means of smelt-water contact in a furnace. A stream of high velocity water from a tube rupture could strike a pool of molten smelt directly and penetrate below its surface. In another case, smelt from a pool could collapse a dam of black ash and run into a pocket of water in the ash bed. The residence time of a water pocket in a hot ash bed could be prolonged by the insulating effect of black ash floating on its surface. This floating ash would not prevent penetration of dense molten smelt into the water pocket beneath. Thus, depending on mixing geometry of the two fluids inside the furnace, either a high or low smelt-to-water ratio could be envisioned. It should be noted that steam per se has never been known to cause smelt explosions. It is commonly employed to prevent dissolving tank explosions by shattering the smelt into small (marble sized) particles before it strikes water in the dissolving tank. Thus, the form of water contacting molten smelt is one variable which determines whether explosions occur.

Conclusions from the present study to date agree with the physical explosion concept of several earlier studies[1,2,3,4]. A physical mechanism also seemed to fit the circumstances better in several recovery furnace explosions which have occurred under

full steaming load when water was introduced into the furnace cavity. The wide variety of molten materials throughout industry which quench explosively in water lends additional credence to a physical explosion mechanism. For example, masses (rather than small particles) of inert molten materials like cobalt, nickel, chrome steel, sodium chloride, sodium hydroxide, and sodium carbonate containing 15% sodium chloride, explode violently on contact with water. Molten aluminum behaves similarly. None of these materials contains sulfides. By contrast many molten materials like sodium carbonate do not explode on contact with water under any known condition or temperature level. Composition of the molten material, therefore, is evidently important in determining whether explosions occur but this may be due to the physical strength of the solidified shell or encapsulating tendency of certain smelt compositions rather than their ability to react chemically with water to produce combustible gases. Thermal dissociation of water into hydrogen and oxygen due to heating to maximum observed smelt temperature, about 2000°F, has been shown by others to yield an insignificant proportion of hydrogen, 0.0084%, at one atmosphere pressure. Only 1.51% hydrogen is formed at 3500°F by heating.

The Encapsulation Mechanism of Explosion

The explosion of combustible gas-air mixtures is a much-studied and comparatively well understood process. There is ample but less publicized evidence in scientific literature, however, that the rapid (1-3 millisecond range or less) release of steam at very high pressures (12,000 to 23,000 psi or higher) can create spherical air shock waves that do tremendous damage even at considerable distances (175 feet or more) away from the explosion site. These waves, which travel at speeds greater than that of sound, can be reflected from a strong, solid barrier below and reinforce the original wave moving upward in the opposite direction. Thus the resulting pressure on the barrier beneath might be only about half that on structures above.

Based on the concepts of Mr. George Long and Dr. Leo F. Epstein, the encapsulation model of Figure 2 is presented. It shows a small quantity of liquid water encapsulated by a much larger one of molten material. This diagram was prepared for molten metal quenching in a relatively large quantity of water, but may apply to other molten materials like kraft smelt. External water-smelt contact would freeze a relatively thick external shell of smelt. The encapsulated water would freeze a somewhat thinner internal layer of smelt. If a relatively small amount of water were introduced below the surface of a large quantity of smelt,

only one frozen smelt shell would be created. Force is necessary to inject water below the surface of smelt since smelt is more than twice as dense as water. Contact of water with the bottom of the container does not seem to be essential for an explosion. Initial heat transfer between smelt and water would be very rapid. It would be slowed as nucleate boiling was transformed into film boiling. Maintenance of nucleate boiling over a critical time period may be necessary for an explosion to occur. As the shell (or shells) of frozen smelt ruptured due to very rapid pressure buildup, a large volume of steam would be liberated with explosive violence shattering the smelt into fine particles. This would effect an even greater rate of heat transfer to any residual water which had not flashed into steam by the sudden release of pressure. A furnace-rending shock wave is believed to be produced by the process under certain conditions. Calculations by others have indicated that shock waves, equivalent to those from detonating 1-2 pounds of TNT, have been generated in some smelt-water furnace explosions.

The quantity of water involved has been of considerable interest to the writer. Calculations based on 18 grams of water, roughly one tablespoonful, encapsulated by molten smelt showed that it could produce 23.3 gallons (approx. 3 cu. ft.) of steam at 1500°F. and atmospheric pressure. The water would expand 1700 times by conversion to steam at 212°F. and 2.92 times more by heating the steam to 1500°F., for a total multiplication of 4960. Pressure inside the smelt-encased capsule of water would likewise be multiplied by a factor of 4960 if no expansion were allowed. Thus a maximum internal pressure of 4960 atmospheres (72,800 psi) could result in the capsule under these conditions if the shell(s) were strong enough to withstand this pressure. The great difference in pressure increase generated by the water, 72,800 psi, compared with that by the same volume of steam, 44.1 psi, in heating from 212°F. to 1500°F may account for their radically different behavior in molten smelt. Composition of the smelt would influence its freezing point and the thickness and strength of the frozen encapsulating shell. It may be that the stronger this shell, the more violent the explosion. Heat transfer rate (which is believed to govern the tendency to explode) would also be affected by the relative masses of smelt and water, the initial temperatures of both, and presence in the encapsulated water of dissolved materials like gases (or those which create gases on heating), surface active agents, or inorganic salts.

Thus, theoretically, large PV (pressure-volume) forces, created by the explosive generation of steam from a relatively small amount of water, may produce equipment-destroying shock waves. The noise and visible damage effects would probably be indistinguishable from those of a combustible type gas explosion, except that no flame would be produced.

Apparatus and Test Method

The method and apparatus used in experiments described in this report are essentially the same as those for direct-quenching work described by Dr. A. L. Plumley in the first report except that water was injected with the tip of the water-introducing tube directly above rather than below the surface of the smelt. The following quench procedure was standardized. A 350 g. charge of smelt, made from pure dried sodium carbonate and sodium sulfide was placed in a graphite crucible in an electrical resistance furnace and heated to 1600-1900°F. This charge created a 1-3/4" depth of molten smelt. A 27% concentration of sodium sulfide (34.3% TAPPI sulfidity) was used for most experiments but 24% (30% sulfidity) was employed in some of the latter ones to compare results at a lower sulfide concentration.

The crucible of molten smelt in its steel holder with long handle was placed in the plywood explosion barrier and a thermocouple was inserted. A recorder traced smelt temperatures during water additions. A succession of small slugs of room temperature distilled water was injected forcibly into the smelt by hypodermic syrigne so that each would penetrate below the surface of the smelt. A 10-35°F drop in smelt temperature was produced by each addition. Water was conducted from the syringe to the smelt by a 6' long 1/8" I.D. stainless steel tube whose outlet end was placed 1/2" to 1" above the smelt surface. Each quenching experiment was observed through a double 30" x 14" pane of safety glass by at least two people, an operator who added the water, and a gas sampler who withdrew cumulative gas samples taken after each water addition before a major explosion occurred. Samples taken after an explosion showed only minute traces of hydrogen due to dilution and dissipation of product gases and/or chemical reaction. Gas samples were drawn from directly above (1") the surface of the smelt and lead into a 250 ml pipet by a stainless steel tube. Analyses were made on a Perkin-Elmer 154D gas chromatograph. Peaks for H_2, CO, CO_2, and air constituents have been observed. No other gases have been shown. A third safety window on the wall facing the door was provided for guest observers. About 30-60 seconds delay between successive water additions was allowed for evaporation of water from the surface (or until an explosion occurred) and for proper registration of smelt temperature by the recorder. When no explosion occurred, the water boiled vigorously but inaudibly on the hot surface of the smelt. Initial explosions rarely occurred on the first injection of water. Most often they took place during the fifth to eighth additions. Some were delayed until the tenth to twelfth, but these were usually reduced in intensity. When an explosion occurred, there was only a slight delay (1-2 seconds) following water addition. Water injections were continued (a) as long as smelt was left in the crucible or (b) until the remaining smelt had solidified. Several violent explosions (only one from an injection) often resulted

from a crucible of smelt, but the first one was usually the most violent. Violence varied almost directly with the volume of individual water injections. Three milliliter injections of liquids are preferred since both 4.0 and 5.0 ml ones in some cases caused explosions violent enough to open up corner seams of the plywood barrier and thereby create a safety hazard to operating personnel.

The intensity of explosions was gauged as mild, moderate, and violent. The moderate ones sounded much like the sharp crack from a .30 caliber rifle and emptied most of the smelt from the crucible. Violent ones produced an ear-ringing shotgun blast which often shattered the graphite crucible into 1" diameter chunks and plastered the smelt against the metal-sheathed ceiling of the barrier. The crucibles used were of strong, dense, relatively non-porous graphite about 1/2" thick. Considerable force would be required to crush them in this manner. Paper thin sheets of solidified smelt floated down past the observation windows soon after these explosions. An acrid smell which some have characterized as "like firecrackers" was produced from both moderate and violent type explosions. This odor was not like hydrogen sulfide. It has not yet been conclusively identified. A total of 111 quenches to date have been run, 33 of which were described in the first report. Only key ones are presented in the current review.

Experimental

(a) Effect of Smelt-to-Water Ratio

It has now been established that kraft smelt and water react explosively over a wide range of proportions. Ratios of 10 to 500 parts of smelt to one of water have caused strong explosions in the present study while the previous investigations showed that as little as .005 part or less of smelt to one of water gave equally violent underwater explosions.

(b) Physical versus Chemical Reaction

There are generally two ways to determine whether a reaction is chemical or physical. One is to measure the energy release of a system and decide whether more was released (by chemical reaction) than was present as sensible heat in the reactants. With the present system we need to know whether energy has been released by a chemical reaction or transferred from smelt to water. In current experiments the addition of water invariably appeared to remove heat from the smelt rather than release heat by chemical reaction. An easier way to resolve the question experimentally is by determining whether the products of the

reaction in question are of different chemical composition than the reactants, and if so, the proportion changed, since both physical and chemical mechanisms could be responsible for these explosions. Suitable equipment is needed, however, to contain the products of an explosive reaction and to exclude other materials, for instance oxygen, which might react chemically with a product of smelt-water contact like hydrogen.

A spherical test barrier described in a later section of this report is ideally suited to this purpose and will be used for the phases of study which require close control of atmosphere. Crude gas-inerting experiments in the plywood barrier were unsuccessful since oxygen was reduced to only about 10%. Decrease in sodium sulfide content by explosions have been measured and found to be in the order of 1-2%, but here again the atmosphere cannot be adequately controlled and results are not reliable. It may prove that this sulfide merely oxidized to sulfate by contact with air.

Hydrogen measurements may suffer some of the same difficulties but are believed indicative since gas samples were taken in the crucible immediately following water addition. They should represent gases sampled from a fairly inert steam atmosphere. Hydrogen produced by injecting small amounts of water into molten smelt at temperatures from about 1400 to 1900°F was very low, in all cases below the explosive limit in dry air (about 5%) and in all other cases except one, below 1.2%. Presence of water vapor in air is known to increase the proportion of hydrogen necessary for an explosion. For instance when 60% of water vapor is present at 187 F. the limit raises to 10%.(5) It generally ran 0.1 to 0.8%. A quench of 1600°F pure sodium carbonate (Run 34) to calibrate possible water reaction with the graphite crucible gave no hydrogen. Smelt temperature was boosted to 1891°F on one quench (Run 45) and hydrogen was the highest of any experiment to date, 4.5%. Smelt temperature is evidently important in determining rate of the hydrogen producing reaction(s).

Temperatures of smelt out of the exit end of the spout of a Maine kraft mill recently measured 1440°F. Smelt in the center of a Finnish kraft mill spout ran 1470° while smelt in dammed-up pools of the bed ran 1970-2010°F when measured by a thermocouple attached to an iron rod and immersed in the smelt. Thus, even a 2000°F smelt temperature seems reasonable if applied to "pooled" rather than normal run-off smelt.

No flash or other visible evidence of a gaseous explosion has been noticed in the 111 quenches to date although many have been observed in the dark by three or more people. While hydrogen can burn with an almost invisible flame, it would be expected to be colored a luminous yellow by the ample supply of sodium compound dust supplied by the explosion. These observations, however, do not constitute scientific proof. Experiments in a wholly inert atmosphere would be necessary to decide this question

conclusively. We do know, however, that violent explosions in previous work occurred when molten smelt was 10-12" below the surface of water, which is an ideal inerting medium for gaseous explosions.

(c) Smelt Temperature Required for Explosions

Experiments in the plywood barrier have allowed easy, practical, determination of a number of fundamental characteristics of the explosive smelt-water reaction. For instance, it was learned that the high temperature smelt quench, Run 45, which produced 4.5% hydrogen did not explode at elevated temperatures, but took place instead on the 11th four ml addition of water at a smelt temperature of 1512°F. These and other results from a large number of quenches indicated that smelt of 24-27% Na_2S has a critical range of temperatures in which violent explosions occur. Tabulation of the 23 very violent explosions of kraft smelt with water over the course of this study has showed that all occurred in the range 1498°-1670°F. None took place above 1670° or below 1498°F. In Run 36 smelt was air chilled to this range before any water additions. An explosion resulted with only three water injections when the smelt reached 1508°F. In Run 37, smelt of the same composition chilled to 1400°F was still liquid but did not explode with any of six-2 ml water additions before freezing.

A sample of 27% Na_2S smelt was cooled slowly while stirring virgorously with a thermocouple to see if significant phase or viscosity changes took place in this range. None was observed at 1400-1700°F except a slight viscosity increase.

(d) Effect of Dissolved Salts

It was reasoned that addition of dissolved salts to the quench water would increase the initial heat transfer rate between smelt and water and hence alter the explosive reaction. Runs 35 and 38 were made to calibrate characteristics of the smelt and to see if preheating the injection water would alter quenching behavior. Preheating had no significant effect. Run 39 employed 10% aqueous sodium carbonate for quenching instead of distilled water. No decided change in quenching violence was noted here. The 15% solution in Run 40 ameliorated explosions and raised the maximum smelt temperature at which explosions occur from 1670 to 1781°F.

In Run 41 the 5% NaCl solution increased violence and also boosted smelt explosion temperature to 1720°F. The 15% NaCl solution quench, Run 42, gave mild pops on each of 18 injections of 2 ml each. From these limited experiments it would seem that dilute salt solutions resulted in more violence than the more concentrated ones. Thus the presence of dissolved salts, even those containing no sulfides, evidently influenced smelt-water reactions.

(e) Effect of Surface Active Agents

It was reasoned that if smelt-water explosions were due primarily to a heat transfer mechanism, they would be influenced by presence of surface active agents which promote more intimate contact by better wetting of hot solid surfaces. Maximum reduction of surface tension of water by many surface active agents occurs at concentrations as low as 100 parts per million (0.01%). Several were used in quench water to determine their effects. Run 43 showed that 4 ml injections of room temperature 0.01% Aerosol OT in water did not noticeably retard explosions. When heated to 160°F, however, the same solution in Run 44 delayed the explosion, greatly reduced its force, and made it occur at a temperature (1363°F) much lower than normal. Some surface active agents did not have this property consistently. Run 45 showed that a hot 0.01% solution of L1159, a highly stable surface active compound with fluorocarbon tail, did not prevent an explosion in this case. In a duplicate run at lower smelt temperature it had prevented violence entirely. Evidently all results should be checked thoroughly by replicate experiments. The results to date, however, indicate that surface active agents do strongly modify quenching behavior of molten smelt.

(f) Effect of Gas-Producing Salts in the Quench Water

The presence in quench water of a dissolved salt which decomposed by heating at temperatures below the boiling point of water might provide a gas blanket between the water and molten smelt. This would be expected to retard heat transfer and hence encapsulation type explosions. Ammonium bicarbonate which starts to decompose into ammonia, carbon dioxide, and water at about 150°F seemed a good candidate for study. A 1% solution in water, Run 46, seemed to intensify explosive force when injected into smelt. This behavior paralleled earlier experience with other dilute salt solutions. At 5% and 20% concentrations in Runs 47 and 48, however, the ammonium bicarbonate effectively prevented explosive violence. Almost an inch depth of rapidly moving large bubbles was produced on the surface of the smelt on each addition of solution at either concentration. Continued injections rapidly froze a crust of solid smelt on the surface of the molten material.

Run 49 was made with 10% urea solution. This material was chosen because it is composed of the same elements as ammonium bicarbonate, would have some of the same thermal decomposition products, and is more stable. It has a decomposition point above 270°F. Violence was increased by urea, which indicated that production of gaseous decomposition products by ammonium bicarbonate was involved in explosion inhibition.

(g) Effect of Black Liquor Addition

It was decided to test the effects of quenching by black liquor of various strengths as might occur in a furnace. Four ml injections of kraft black liquor of 10%, 25%, 35%, and 50%

solids content were made into molten 27% Na_2S smelt, Runs 50, 51, 52, 53. Experiments with each liquor concentration were made in duplicate. Explosions were produced with 10%, 25%, and 35% solids liquors but not with the 50%. High viscosity of the 50% liquor complicated the results. It was impossible to inject this viscous fluid, even when hot, beneath the surface of the molten smelt using current equipment. It quickly formed a thick layer of char through which further liquor would not likely penetrate in quantity. Hydrogen proportions from pyrolysis of all these concentrations was surprisingly low, 0.18 to 0.90%. Experiments with the 50% black liquor bear repeating due to its frequent use in rapidly cooling down hot furnace beds. Initial smelt temperature for this run was lower than preferred.

(h) Effect of Surface Addition of Water

A batch of 27% sodium sulfide smelt at 1663°F, Run 54, was quenched by ten successive 2 ml portions of water added at low velocity so that it would have little tendency to penetrate below smelt surface. Six mild pops, but no explosion resulted. These results confirmed Dr. Plumley's findings that water must be forced under the surface of molten smelt to cause explosions.

(i) Quench of Sulfide-free Smelt

It became of interest next to see if addition of sulfide-free sodium compounds to sodium carbonate could make a molten solution which quenched explosively on injection of small amounts of water. Sodium chloride was chosen since it is a normal constituent of kraft smelt in Pacific Northwest mills which pulp salt-water borne logs. This material was also responsible[1] for violent dissolving tank explosions in a Pennsylvania soda pulp mill. Although quite thermally stable, this salt was found by previous study to have an intensifying effect on kraft smelt dissolving tank explosions. Sodium chloride in small proportion has the property of lowering ash and smelt melting points, which may be a function of its relatively low molecular weight. Examination of Runs 55, 56 and 57 showed that 5% sodium chloride did not make the mixture explode, but 15% and 20% in sodium carbonate were violent-quenching compositions. These compositions took place at temperatures (1442 and 1338°F) which were considerably below the kraft smelt explosion range. It is evident from the experiments that molten materials which contain no sulfides can, like kraft smelt, explode violently on injection of small portions of water below their surface.

(j) Influence of Sodium Sulfide on Some Physical Properties of Kraft Smelt

It had been postulated that addition of sodium sulfide would alter the physical properties of sodium carbonate when melted with it. Small cylinders of sodium carbonate and sodium carbonate with several proportions of sodium sulfide were melted and

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The cylindrical specimens were compressively loaded to failure in the tensile testing machine. All specimens failed quite abruptly, usually by fracturing longitudinally into several fragments. Results are shown in Table 2 which is appended.

Although casting techniques must be refined in order to avoid shrinkage cavaties and other flaws which impair strength and consistency, the data show that even 10% sodium sulfide imparted a remarkable increase of compression strength, 1470% to sodium carbonate. Chemical analysis of the cooled castings showed that no significant change in composition had occurred during the melting process. Sodium carbonate cast under the same conditions was comparatively weak with a compression strength of 1080 psi. These data will be checked when castings with less flaws are made. The same techniques are being applied to sodium chloride-sodium carbonate melts. From these experiments there can be no doubt that inclusion of sodium sulfide in sodium carbonate greatly increases the mechanical strength of the solidified smelt.

Discussion and Tentative Conclusions

Most of the data to date underline a physical rather than chemical mechanism for smelt-water explosions. Among the supporting evidence presented in this report can be listed the following:

1. Explosions took place only when liquid water was placed beneath the surface of molten smelt, even with highly explosive smelt compositions.

2. Explosions occurred over a broad range of smelt to water ratios which is not characteristic of chemical reactions.

3. Hydrogen or any other combustible product of smelt-water reaction was never found in evolved gases in high enough proportions to produce an explosion in air--even dry air.

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3. Hydrogen or any other combustible product of smelt-water reaction was never found in evolved gases in high enough proportions to produce an explosion in air--even dry air.

4. Water injections always resulted in a decrease in smelt temperature which is characteristic of either no chemical reaction or an endothermic one.

5. Explosions with water and smelt occurred in a definite range within the molten range of smelt. They did not occur, however, if smelt temperature was above 1670°F. It was postulated that heat transfer rate may be critical in this range. Perhaps nucleate boiling above 1670°F became transformed too rapidly into film boiling to effect the heat transfer rate necessary for an explosion.

6. Dilute solutions of inorganic salts in the quench water increased violence and raised the smelt temperature at which explosions occurred. Concentrated solutions ameliorated explosions.

7. Hot, very dilute solutions of some surface active agents retarded or prevented explosions.

8. A gas-producing salt, ammonium bicarbonate, in quench water effectively prevented explosions at 5-20% concentration. Thermal decomposition of this material would be expected to cool the smelt rapidly due to gas evolution and to blanket encapsulated portions of water. (The gases evolved are inert and would also tend to prevent explosion of any flammable gases produced from smelt-water interaction.)

9. Sulfide-free smelts like sodium carbonate with 15% and 20% sodium chloride also quenched explosively. With these compositions it is difficult to postulate chemical reactions with water which produce large proportions of hydrogen.

10. Incorporation of only 10% sodium sulfide in sodium carbonate increased its compression strength by a 14 fold factor. The role of sodium sulfide as an encapsulation wall strengthener may account for its ability to increase explosive violence in smelt quenching.

It was encouraging to learn that pyrolysis of 50% black liquor produced so little hydrogen. This experiment will be repeated and checked for other combustible gases. The results, however, are in some measure substantiated by field experience. We are aware of no instance in which the introduction of strong black liquor alone into a chemical recovery furnace has resulted in a furnace-damaging explosion.

Although explosions due to encapsulation of water in kraft smelt seem plausible from the work of previous experimenters in other fields and from that described in this report, we do not intend to assume it applies or is governing under all furnace conditions. The relative contributions of energy release from explosion of combustible gases and encapsulation at various temperatures must be carefully assessed before a valid conclusion about explosion mechanism(s) can be reached. Such a distinction, however, must await further study in the spherical barricade now being constructed at Chattanooga.

More knowledge about how explosions occur is of more than academic interest. It will greatly accelerate development of a practical remedy for them in operating chemical recovery furnaces. For instance, if explosions of combustible gas are responsible for the major furnace damage, gas inerting experiments would be in order. If a physical encapsulating mechanism were governing, however, inerting of furnace atmospheres would be ineffectual and other means of preventing explosions or decreasing their violence must be sought. Due to the often substantial time lag (sometimes as long as several hours) between observation of a tube rupture and the resulting explosion, we believe a major goal of this study should be the development of a preventative shutdown procedure which could be initiated during this period of grace.

Spherical Barricade and Accessory Equipment

Design details of a high pressure barricade and instrumentation with which precise smelt-water contacting experiments can be made have been finalized. A strong, rigid sphere was decided upon as the proper container for explosion experiments. It will allow control of the atmosphere used so that the relative parts played by combustion of flammable gases from quenching and by physical encapsulation of water can be assessed. The energy liberated by expanding gases and by shock wave can be measured. The gaseous and solid products of the explosions can be analyzed quantitatively so that the nature and extent of chemical reaction(s) can be studied. The explosions can be observed by camera at close range. Another important advantage of the spherical barricade lies in its use to scale up remedial measures considerably beyond the size accommodated safely by the plywood barricade. A safety factor of 18 has been designed (using 200 g. quantities) assuming that all reactants are vaporized at 1830°F. (1000°C.). The walls will stand 500 psi at 650°F but shell temperature will be considerably lower since smelt will be melted outside the vessel. The girth and flange seams will be x-rayed to insure safety. It will be hydrostatically tested at 750 psi. The size chosen is a convenient one since the same dies used for manufacture of boiler drum heads in C.E.'s Chattanooga shops

can be employed for the two hemispherical halves. This will save expense and time. The 49" OD sphere will be made of 11/16" thick low carbon steel (SA 212 Grade B). It will have five 6" flanges for mounting a rupture disc, a piezoelectric pressure transducer, camera, and a sight glass for visual observation (by mirror). It has a 16" quick-closing manhole to allow placement of quenching vessels and other test equipment.

A trip was made to the Kistler Instrument Co., at Clarence, N. Y. to gain first hand information about the application of piezoelectric quartz high pressure transducers to this system for measuring explosion shock waves. The transducer ordered allows measurement of dynamic pressures up to 30,000 psi with very fast rise times, as little as 2.5 microseconds (millionths of a second). A charge amplifier and power amplifier for boosting current from the transducer to the level necessary for recording on C.E.'s Visicorder were also ordered. Resistance type heating furnace for the melting of smelt have proven unsatisfactory due to the pronounced tendency of smelt and its vapors to attack both refractory and nichrome heating elements. In addition, the melting time for a 350 g. charge is excessive, averaging 1-2 hours. The exact crucibles and smelt composition were tried in several induction furnaces. The 10 KW size model was ordered and is being installed currently. Heating time to 2000°F with an uninsulated crucible was less than 10 minutes. The water-cooled current-carrying coils run at less than 130°F, hence corrosion by molten salts will be eliminated. This furnace will eliminate a major bottleneck in the proposed studies.

Future Work

Work in the immediate future will include further investigations of the strength and structure of smelts containing sodium chloride and sodium sulfide. Further study of the inhibiting action of ammonium bicarbonate, 50% black liquor, and surface active agents will be made since it may provide a clue to a practical remedy to smelt explosions in furnaces, or a safer shut down procedure. Concentrated black liquor quenching will be emphasized since it is readily available and appears not to cause explosions. Key experiments will be run in replicate to increase confidence limits in the data. Various parts of the apparatus and instrumentation for the spherical test barrier will be assembled and tested as they arrive.

Wharton Nelson

WHARTON NELSON
Senior Project Engineer
August 28, 1964

TABLE 1

Results from New Quenching Experiments

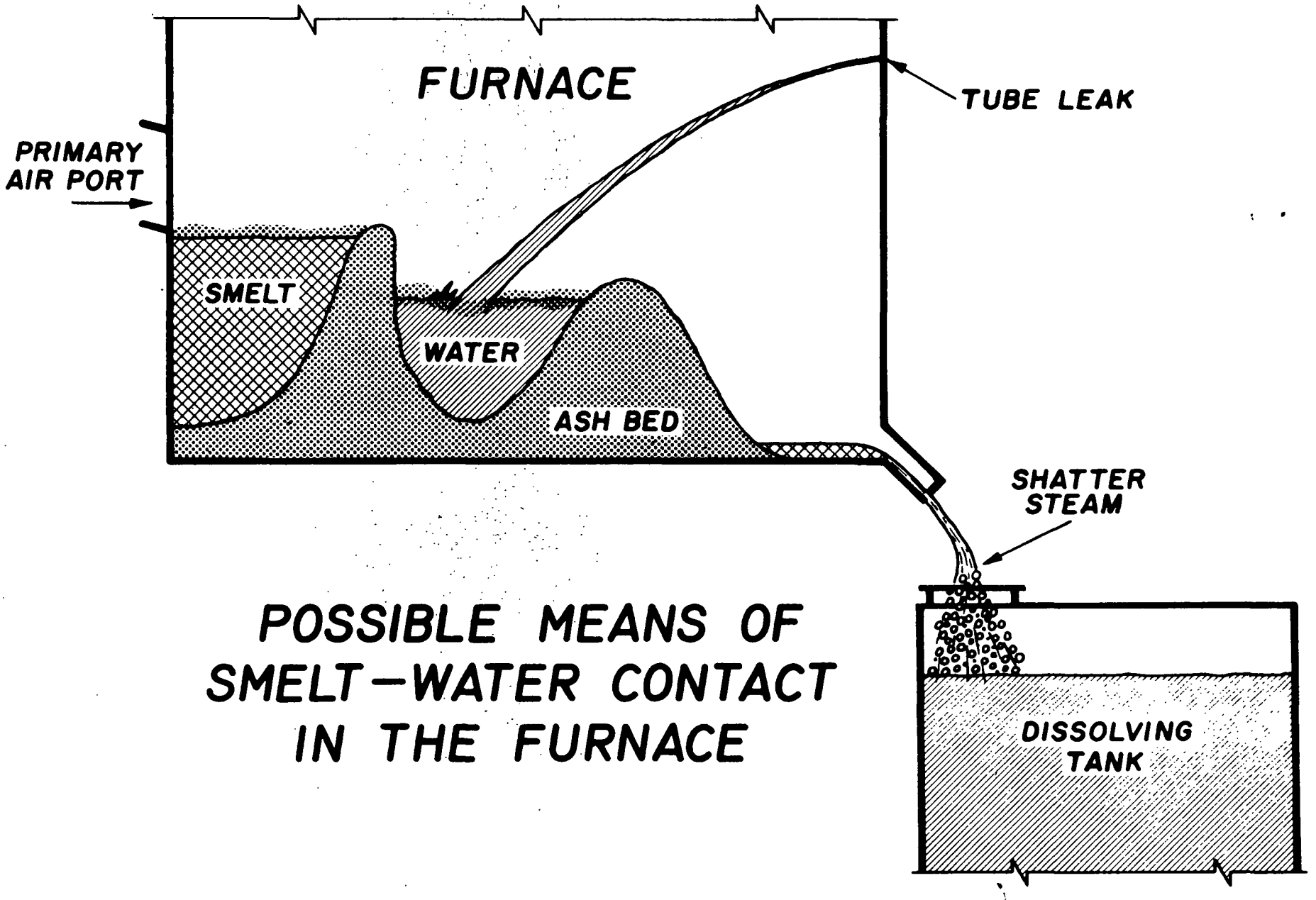
Run No.	Smelt % Composition	Quench Liquid	Results	Init. Smelt Temp.	Smelt Temp. for Explosions	% H_2
34	100% Na_2CO_3	Water - 3 ml.	No violence after 20 injections	1600	None	0
35	Smelt A* - Blank	Water - 4 ml.	Mild Expl,on 3rd inj.;very** violent 7	1685	1658, 1538	-
36	Smelt A	Water - 3 ml.	Violent expl. on 3	1565	1508	0.14
37	Smelt A	Water - 2 ml.	No expl.on any injection of 6	1400	None	0
38	Smelt A	180°F. Water - 4 ml.	Violent** expl. on 6	1676	1503	0.61
39	Smelt A	10% Na_2CO_3 soln.-2 ml.	Violent expl. on 4 and 5	1690	1623, 1565	0
40	Smelt A	15% Na_2CO_3 soln.- 2 ml.	Mild expl. on 1 and 9	1781	1781, 1547	0.51
41	Smelt B	5% NaCl soln.- 3 ml.	Violent** expl. on 1	1720	1720	0.03
42	Smelt A	15% NaCl soln.- 2 ml.	Mild pops on each of 18 injections	1618	1618, 1433	0.42
43	Smelt A	0.01% Aerosol OT - 4 ml.	Violent expl. on 6	1640	1499	0
44	Smelt A	160°F.-0.01% Aerosol OT-4ml.	Mild expl. on 16	1717	1363	0
45	Smelt A	170°F.-0.01% L1159-4 ml.	Violent**expl.on 11, moderate 12	1891	1512	4.5
46	Smelt A	1% NH_4HCO_3 soln.- 4 ml.	Extremely** violent on 3	1591	1555	0
47	Smelt A	5% NH_4HCO_3 soln.- 4 ml.	No expl. on any of 15	1740	None	0.84
48	Smelt A	20% NH_4HCO_3 soln.- 4 ml.	No expln. of any of 18	1591	None	0.36
49	Smelt A	10% Urea soln. - 4 ml.	Extremely** violent on 2	1654	1613	0.60
50	Smelt A	10% Kraft Black Liquor-2ml.	Moderate expl. on 4	-	-	0.20
51	Smelt A	25% Kraft Black Liquor-4ml.	Expl. on 6, 8, and 9	1708	1501,--,--	0.90
52	Smelt A	35% Kraft Black Liquor-4ml.	Expl. on 2 and 3	1520	1485, 1416	0.18
53	Smelt A	50% Kraft Black Liquor-4ml.	No expl. on any injection	1503	None	0.66
54	Smelt A	Water-2 ml., Added Gently	No expl.-Slight pops on 3,4,5,6,8,9	1663	None	0
55	5% NaCl,95% Na_2CO_3	Water - 3 ml.	No violence - 13 injections	1686	None	0
56	15% NaCl, 85% Na_2CO_3	Water - 2 ml.	Violent expl. on 9th injection	1620	-	0
57	20% NaCl, 80% Na_2CO_3	Water - 3 ml.	Violent expls. on 5th and 6th inj.	1538	1442, 1338	0.18

*Smelt A - 27% Na_2S in Na_2CO_3
Smelt B - 24% Na_2S in Na_2CO_3

**These explosions shattered crucible.

TABLE II

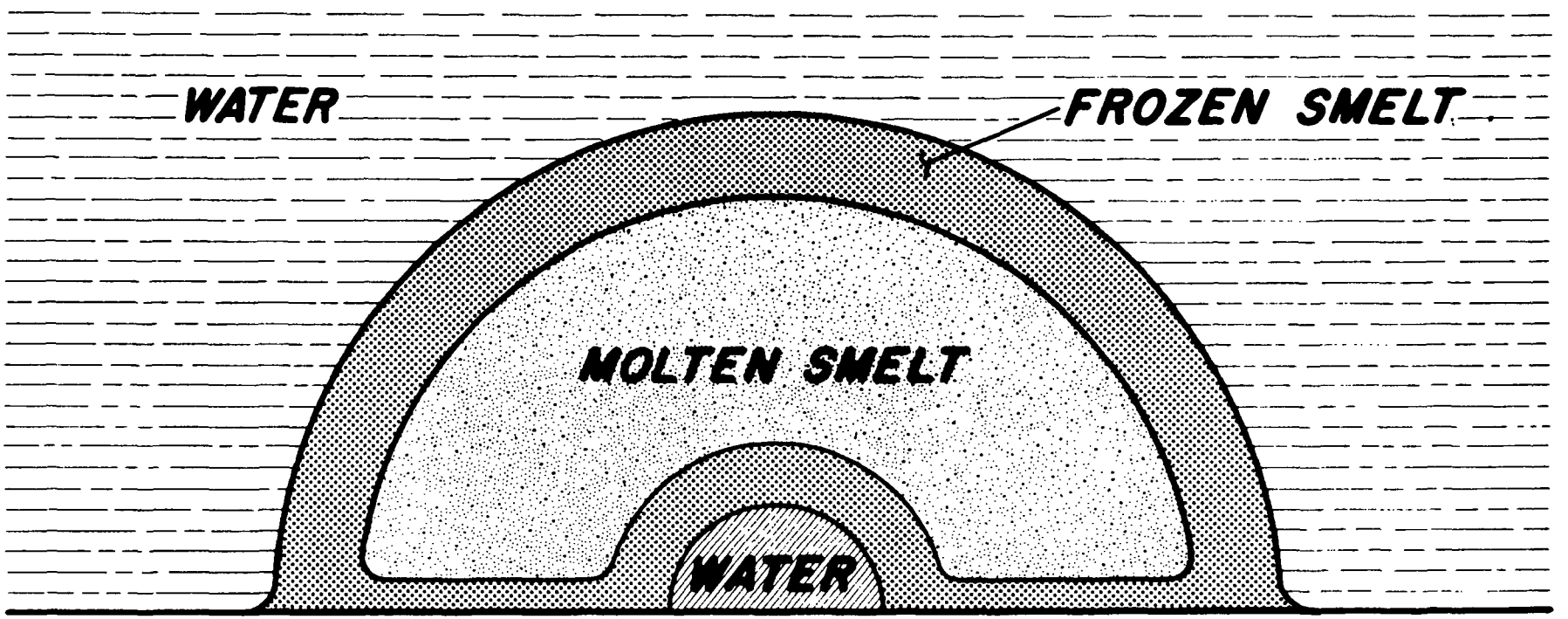
Sample Number	Composition % Na_2CO_3	% Na_2S	Appearance of Structures at 40X	Compression Test Load (lbs)	Strength (psi)	Comment on Failures
1	100	0	Dense, translucent crystallites randomly oriented in outer portion and radially oriented in vicinity of shrinkage cavity. Uniformly white in color.	320	1,080	Cracked both longitudinally and transversely into several irregularly shaped fragments.
2	90	10	Dense very fine crystallites. Uniformly light pink in color. This specimen was free of central shrinkage cavity.	4015	15,900	Cracked longitudinally into two nearly equal fragments through an internal defect, presumably graphite powder from mold.
3	80	20	Outer zone dense, fine crystallites darker pink in color than No. 2. Inner zone - radially oriented, dendritic crystals adjacent to shrinkage cavity. Uniform dispersion of very fine dark particles.	4120	15,400	Cracked longitudinally into several fragments through shrinkage cavity.
4	70	30	Very fine distribution of dark particles within a pink matrix.	5570	19,800	Cracked longitudinally into several fragments. Fracture surfaces were granular in appearance.



POSSIBLE MEANS OF SMELT–WATER CONTACT IN THE FURNACE

FIG. 1

(theoretical model)



Physical Encapsulation Explosions

FIG. 2